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Biodiesel production through the use of different sources and characterization of oils and their esters as the substitute of diesel: A review

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ABSTRACT

The world is confronted with the twin crises of fossil fuel depletion and environmental degradation. The indiscriminate extraction and consumption of fossil fuels have led to a reduction in petroleum reserves. Petroleum based fuels are obtained from limited reserves. These finite reserves are highly concentrated in certain region of the world. Therefore, those countries not having these resources are facing a foreign exchange crisis, mainly due to the import of crude petroleum oil. Hence it is necessary to look for alternative fuels, which can be produced from materials available within the country. Although vegetative oils can be fuel for diesel engines, but their high viscosities, low volatilities and poor cold flow properties have led to the investigation of its various derivatives. Among the different possible sources, fatty acid methyl esters, known as Biodiesel fuel derived from triglycerides (vegetable oil and animal fates) by transesterification with methanol, present the promising alternative substitute to diesel fuels and have received the most attention now a day. The main advantages of using Biodiesel are its renewability, better quality exhaust gas emission, its biodegradability and the organic carbon present in it is photosynthetic in origin. It does not contribute to a rise in the level of carbon dioxide in the atmosphere and consequently to the green house effect. This paper reviews the source of production and characterization of vegetable oils and their methyl ester as the substitute of the petroleum fuel and future possibilities of Biodiesel production.

Contents

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1. Introduction

The depleting reserves of fossil fuel, increasing demands for diesels and uncertainty in their availability is considered to be the important trigger for many initiatives to search for the alternative source of energy, which can supplement or replace fossil fuels.

One hundred years ago, Rudolf Diesel tested peanut oil as fuel for his engine for the first time on August 10, 1893 [1]. In the 1930s and 1940s vegetable oils were used as diesel fuels from time to time, usually only in emergency. The first International conference on plant and vegetable oils as fuels was held in Fargo, North Dakota in August 1982. The primary concern discussed were the cost of fuel, the effect of vegetable oil fuels on engine performance and durability and fuel preparation specification and additives. Oil production, oil seed processing and extraction also were considered in this meeting [2]. Vegetable oils hold promise as alternative fuels for diesel engines [3,4]. But their high viscosities, low volatilities and poor cold flow properties have led to the investigation of various derivatives. Fatty acid methyl esters, known as Biodiesel, derived from triglycerides by transesterification with methanol have received the most attention [5,6].

The name Biodiesel was introduced in the United States during 1992 by the National Soy diesel Development Board (presently national bio diesel board) which has pioneered the commercialization of Biodiesel in the United States. Biodiesel can be used in any mixture with petroleum diesel as it has very similar characteristics but it has lower exhaust emissions. Biodiesel has better properties than that of petroleum diesel such as renewable, biodegradable, non-toxic, and essentially free of sulfur and aromatics. Biodiesel fuel has the potential to reduce the level of pollutants and the level of potential or probable carcinogens [7]. Ma et al. [8] stated that Biodiesel has become more attractive recently because of its environmental benefits and fact that it is made from renewable resources. The raw materials being exploited commercially by the Biodiesel are the edible fatty oils derived from rapeseed, soybean, palm, sunflower, coconut, linseed, etc. [9]. In recent years, research has been directed to explore plant based fuels, have bright future [10]. This chapter focused on the source of oils, problems associated with the use of oils, production of Biodiesel from non-edible oil, Physical and chemical properties of oils and esters; advantages, disadvantages and challenges.

2. Source of Biodiesel

Alternative diesel fuels made from natural, renewable sources such as vegetable oil and fats [11,12]. The most commonly used oils for the production of Biodiesel are soybean [13,14], sunflower [15,16], palm [17], rapeseed [18], canola [19], cotton seed [20] and Jatropha [21]. Since the prices of edible vegetable oils are higher than that of diesel fuel, therefore waste vegetable oils and non-edible crude vegetable oils are preferred as potential low priced Biodiesel sources. Use of such edible oil to produce Biodiesel in India is also not feasible in view of big gap in demand and supply of such oils. Under Indian condition only such plants can be considered for Biodiesel, which produce non-edible oil in appreciable quantity and can be grown on large scale on non-cropped marginal lands and waste lands. Animal fats, although mentioned frequently, have not been studied to the same extent, as vegetable oils because of natural property differences. Animal fats contain higher level of saturated fatty acids therefore they are solid at room temperature [22]. The source of Biodiesel in the form of vegetables oils, non-edible oils, animal fats and some other biomass are listed in Table 1.

The source of Biodiesel usually depends on the crops amenable to the regional climate. In the United States, soybean oil is the most commonly Biodiesel feedstock, whereas the rapeseed (canola) oil and palm oil are the most common source for Biodiesel, in Europe, and in tropical countries respectively [68]. A suitable source to produce Biodiesel should not competent with other applications that rise prices, for example pharmaceutical raw materials. But the demand for pharmaceutical raw material is lower than for fuel sources. As much as possible the Biodiesel source should fulfill two requirements: low production costs and large production scale. Refined oils have high production costs, but low production scale; on the other side, non-edible seeds, algae and sewerage have low production costs and are more available than refined or recycled oils.

The oil percentage and the yield per hectare are important parameters to consider as Biodiesel source. Productions of non edible oil seeds percentage of oil content are given in Table 2.

3. Chemical composition of alternative fuels (oil and Biodiesel) and diesel

From a chemical point of view, oils from different sources have different fatty acid compositions. The fatty acids vary in their carbon chain length and in the number of unsaturated bonds they contain. Fats and oils are primarily water-insoluble, hydrophobic substances in the plant and animal kingdom that are made up of one mole of glycerol and three moles of fatty acids and are commonly referred as triglycerides [70] Fig. 1

Chemically the oil/fats consist of 90–98% triglycerides and small amount of mono and diglycerides. Triglycerides are esters of three fatty acids and one glycerol. These contain substantial amount of oxygen in their structures. When three fatty acids are identical, the product is simple triglycerides, when they are dissimilar the product is mixed triglycerides fatty acids which are fully saturated with hydrogen have no double bonds. Those with one missing hydrogen molecule have one double bond between carbon atoms and are called monosaturated. And those with more than one missing hydrogen have more than one double bond and are called polyunsaturated. Fully saturated triglycerides lead to excessive carbon deposits in engines. The fatty acids are different in relation to the chain length, degree of unsaturation or presence of other chemical functions. Chemically, Biodiesel is referred to as the mono-alkyl esters of long-chain-fatty acids derived from renewable lipid sources. Biodiesel is the name for a variety of ester based oxygenated fuel from renewable biological sources. It can be used in compression ignition engines with little or no modifications [72].

Biodiesel is made in a chemical process called transesterification, where organically derived oils (vegetable oils, animal fats and recycled restaurant greases) are combined with alcohol (usually methanol) and chemically altered to form fatty esters such as

Table 1
Source of oil.

Vegetable oils	Non-edible oils	Animal Fats	Other Sources
Soybeans [13,14,23]	Almond [33]	Lard [22]	Bacteria [1]
Rapeseed [18]	*Abutilon muticum* [34]	Tallow [64]	Algae [1]
Canola [19,24]	Andiroba [35]	Poultry Fat [64]	Fungi [1]
Safflower [15,16]	Babassu [29,30,35]	Fishoil [30,31]	Micro algae [65]
Barley [25]	*Brassica carinata* [36]		Tarpenes [66]
Coconut [23,26,27]	*B. napus* [36]		Latexes [66]
Copra [28]	Camelina [37]		Cooking Oil (Yellow Grease) [64]
Cotton seed [20]	Cumaru [35]		Microalgae (Chlorellavulgaris) [67]
Groundnut [23,28–30]	*Cynara cardunculus* [38]		
Oat [25]	Jatrophacurcas [21,39,40]		
Rice [25,28,31]	*Jatropha nana* [41]		
Sorghum [25]	Jojoba oil [42]		
Wheat [25]	Pongamiaglabra [43,44]		
Winter rapeseed oil [32]	Laurel [23]		
	Lesquerellafendleri [45]		
	Mahua [46,47]		
	Piqui [23,48,49]		
	Palm [17,50–52]		
	Karang [53]		
	Tobacco seed [54–56]		
	Rubber plant [49,57,58]		
	Rice bran [59–62]		
	Sesame [23]		
	Salmon oil [63]		

Table 2
Production of non-edible oil seeds and bio-residues in India [69].

Species	Oil faction (%)	Seed estimate (10^6 tones/y)	Oil (tons/ha/y)
Castor	45–50	0.25	0.5–1.0
Jatropha	50–60	0.20	2.0–3.0
Mahua	35–40	0.20	1.0–4.0
Sal	10–12	0.20	1.0–2.0
Linseed	35–45	0.15	0.5–1.0
Neem	20–30	0.10	2.0–3.0
Pongamia (Karanja)	30–40	0.06	2.0–4.0
Others	10–50	0.50	0.5–2.0
Others	10–50	0.50	0.5–2.0

methyl ester. Chemically, most Biodiesel consists of alkyl (usually methyl) esters instead of the alkanes and aromatic hydrocarbons of petroleum derived diesel.

Oil, ester and diesel have different number of carbon and hydrogen compound. Diesel has no oxygen compound. It is a good quality of fuel. On the other hand, in the case of vegetable oils Oxidation resistance is markedly affected by the fatty acid composition. The large size of vegetable oil molecules (typically three or more times larger than hydrocarbon fuel molecules) and the presence of oxygen in the molecules suggests that some fuel properties of vegetable oil would differ markedly from those of hydrocarbon fuels [3]. Chemical structure of oil, Biodiesel and petroleum diesel are given Table 3.

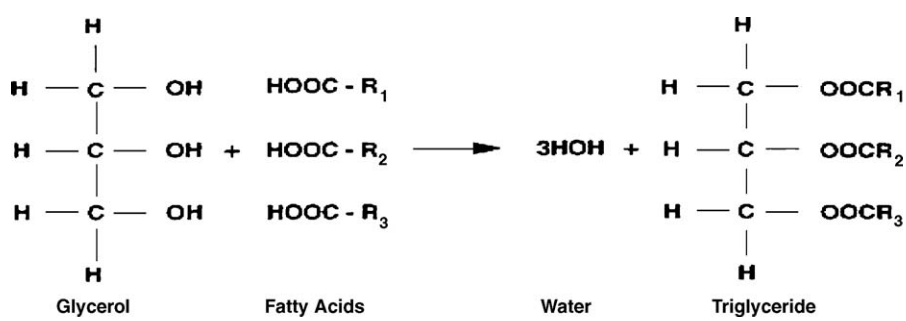


Fig. 1. Chemical structure of vegetable oil [71].

Table 3
Chemical structure of oil,ester and diesel.

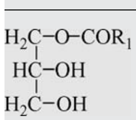
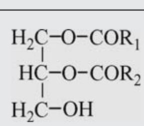
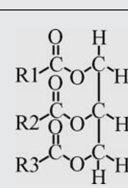
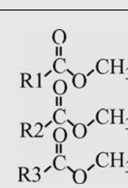
Chemical structure of Monoglyceride	Chemical structure of Diglyceride	Chemical structure of Fat &Oil	Chemical Structure of Ester	Chemical structure of Diesel
				$C_{12}H_{23}$

Table 4
Chemical structure of common fatty acids.

Name of fatty acid	Chemical name of fatty acids	Structure (xx:y)	Formula
Lauric	Dodecanoic	12:0	$C_{12}H_{24}O_2$
Myristic	Tetradecanoic	14:0	$C_{14}H_{28}O_2$
Palmitic	Hexadecanoic	16:0	$C_{16}H_{32}O_2$
Stearic	Octadecanoic	18:0	$C_{18}H_{36}O_2$
Oleic cis-9-	Octadecenoic	18:1	$C_{18}H_{34}O_2$
Linoleic cis-9,cis-12-	Octadecadienoic	18:2	$C_{18}H_{32}O_2$
Linolenic	cis-9,cis-l2,cis-15-Octadecatrienoic	18:3	$C_{18}H_{30}O_2$
Arachidic	Eicosanoic	20:0	$C_{20}H_{40}O_2$
Behenic	Docosanoic	22:0	$C_{22}H_{44}O_2$
Erucle	cis-13-Docosenoic	22:1	$C_{32}H_{42}O_2$
Lignoceric	Tetracosanoic	24:0	$C_{24}H_{48}O_2$

Petroleum based diesel fuels have different chemical structures from vegetable oils and esters. The former contain only carbon and hydrogen atoms, which are arranged in normal (straight chain) or branched chain structures, as well as aromatics configuration. The normal structures preferred for better ignition quality [73]. Diesel fuel can contain both saturated and unsaturated hydrocarbons, but the latter are not present in large enough amounts to make fuel oxidation problem. Petroleum-derived diesel is composed of about 75% saturated hydrocarbons (primarily paraffins including *n*, *iso*, and cycloparaffins), and 25% aromatic hydrocarbons (including naphthalenes and alkylbenzenes) [74]. The average chemical formula for common diesel fuel is $C_{12}H_{23}$, ranging from approximately $C_{10}H_{20}$ to $C_{15}H_{28}$.

Vegetable oils contain fatty acid, free fatty acids (generally 1–5%), phospholipids, phosphatides, carotenes, tocopherols, sulfur compound and traces of water [75]. The fatty acids, which are commonly found in vegetable oils, are stearic, palmitic, oleic, linoleic and linolenic. Table 4 summarizes the fatty acid composition of some vegetable oils [4,33,35,64].

Triglyceride molecules have molecular weights between 800 and 900 and are thus nearly four times larger than typical diesel fuel molecules [76]. The various vegetable oils and esters are distinguished by their fatty acid compositions. In Tables 5 and 6 different fatty acids are shown by their respective number of carbon present in the structure of oils and esters.

Table 5 summarized the fatty acid composition of fifty-one samples of vegetable oils and fat. Twenty one fatty acids are screened in all the samples. The fatty acids which are commonly found in vegetable oil and fat are stearic, palmitic, oleic, linoleic. The other fatty acids which are also present in many of the oils and fats are myristic (tetradecanoic), palmitoleic, acachidic, linolenic and octadecatetranoic. There are many other fatty acids which are also found in oils with the above-mentioned common fatty acids. Lauric fatty acid is present only in bay laurel leaf, coconut, Babassu and Luphea. Myristoleic and ecosenoic fatty acids are found in beef tallow, choice white and poultry fat. Eicosenoic fatty acid is present in beef tallow, choice white, poultry fat, yellow grease and camalina. Behenic, lignoceric fatty acids are detected in peanut kernel and crambe. Erucle fatty acid is found only in three oils, i.e. crambe camellia oil and *Brassica carinata*.

In the oil of Cotton, Tobbaco, rapeseed, safflower, sunflower, Sesame, linseed, palm, corn, soyabean, peanut and rice bran, the content of the fatty acid is different in the same plant species that may be either due to the varital or instrumental difference or in the different parts of plants.

Fatty acid profiles of seed oil methyl esters of 75 plant species having 30% or more fixed oil in their seed/kernel were examined (Table 6). Fatty acid compositions were used to predict the quality of fatty acid methyl esters of oil for use as Biodiesel. Fatty acid methyl ester of oils of 26 species including *Azadirachta indica*, *Calophyllum inophyllum*, *Jatropha curcas* and *Pongamia pinnata* were found most suitable for use as Biodiesel and they meet the major specification of Biodiesel standards of USA, Germany and European Standard Organization [97].

The fatty acid methyl esters of another 11 species meet the specification of Biodiesel standard of USA only. These selected plants have great potential for Biodiesel [81].

4. Processes or method to produce Biodiesel

Considerable efforts have been made to develop vegetable oil derivatives that approximate the properties and performance of hydrocarbons-based diesel fuels. The problem with substituting triglycerides for diesel fuel is mostly associated with high viscosity, low volatility and polyunsaturated characters. These can be changed in at least four ways: pyrolysis, microemulsion, dilution and transesterification.

4.1. Pyrolysis

Pyrolysis is a method of conversion of one substance into another by mean of heat or by heat with the aid of the catalyst in the absence of air or oxygen [98]. The process is simple, wasteless, pollution free and effective compared with other cracking processes. The reaction of thermal decomposition is shown in Fig. 2.

4.2. Dilution

The vegetable oil is diluted with petroleum diesel to run the engine. Caterpillar Brazil, in 1980, used pre-combustion chamber engines with the mixture of 10% vegetable oil to maintain total power without any alteration or adjustment to the engine. At that point it was not practical to substitute 100% vegetable oil for diesel fuel, but a blend of 20% vegetable oil and 80% diesel fuel was successful. Some short-term experiments used up to a 50/50 ratio.

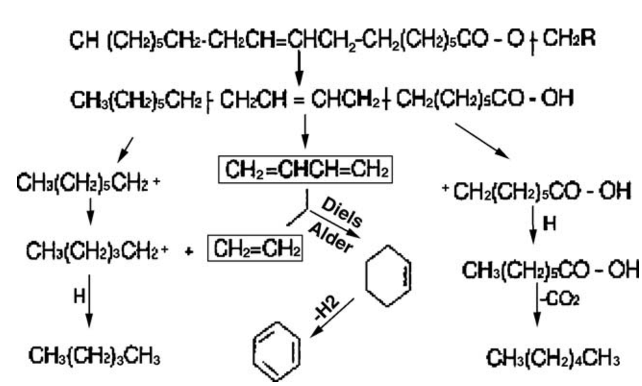


Fig. 2. The mechanism of thermal decomposition of triglycerides [99].

Table 5
Fatty acid composition of oil.

S. No.	Vegetable oil	Fatty acid composition (wt.%)																Reference
		12:0	14:0	14:1	16:0	16:1	18:0	20:0	20:1	22:0	24:0	18:1	22:1	18:2	18:3	18:4	6:0[a], 8:0[b], 10:0[c] and Others	
1.	Cottonseed	–	–	–	28.7	–	0.9	–	–	–	–	13.0	–	57.4	–	–	–	[33]
2.	Cottonseed	–	0	–	28	–	1	0	–	0	0	13	0	58	0	–	–	[3]
3.	Tobacco	–	0.09	–	10.96	0.2	3.34	–	–	–	–	14.54	–	69.49	0.69	–	0.69	[78]
4.	Tobacco	–	0.17	–	8.87	0.0	3.49	–	–	–	–	12.4	–	67.75	4.20	–	–	[79]
5.	Rapeseed	–	–	–	3.5	–	0.9	–	–	–	–	64.1	–	22.3	8.2	–	–	[33]
6.	Rapeseed	–	0	–	3	–	1	0	–	0	0	64	0	22	8	–	–	[3]
7.	Safflower seed	–	–	–	7.3	–	1.9	–	–	–	–	13.6	–	77.2	–	–	–	[33]
8.	Safflower	–	0	–	9	–	2	0	–	0	0	12	0	78	0	–	–	[3]
9.	H.O.Safflower	–	Tr	–	5	–	2	Tr	–	0	0	79	0	13	0	–	–	[3]
10.	Sunflower	–	–	–	6.4	0.1	2.9	–	–	–	–	17.7	–	72.9	–	–	–	[33]
11.	Sunflower	–	0	–	6	–	3	0	–	0	0	17	0	74	0	–	–	[3]
12.	Sesame	–	–	–	13.1	–	3.9	–	–	–	–	52.8	–	30.2	–	–	–	[33]
13.	Sesame	–	0	–	13	–	4	0	–	0	0	53	0	30	0	–	–	[3]
14.	Linseed	–	–	–	5.1	0.3	2.5	–	–	–	–	18.9	–	18.1	55.1	–	–	[33]
15.	Linseed	–	0	–	5	–	2	0	–	0	0	20	0	18	55	–	–	[3]
16.	Palm	–	–	–	42.6	0.3	4.4	–	–	–	–	40.5	–	10.1	0.2	1.1	–	[33]
17.	Palm tree	–		–	35	–	7	–	–	–	–	44	–	14	–	–	–	[35]
18.	Corn marrow	–	–	–	11.8		2.0	–	–	–	–	24.8	–	61.3	–	0.3	–	[33]
19.	Corn	–	0	–	12	–	2	Tr	–	0	0	25	0	6	Tr	–	–	[3]
20.	Tallow	–	–	–	23.3	0.1	19.3	–	–	–	–	42.4	–	2.9	0.9	2.9	–	[33]
21.	Beef tallow		2.73	0.50	22.99	2.86	19.44	0.14	0.33	–	–	41.60	–	3.91	0.49	0.36	–	[64]
22.	Soybean	–	–	–	13.9	0.3	2.1	–	–	–	–	23.2	–	56.2	4.3	0	–	[33]
23.	Soya bean	–	–	–	14	–	4	–	–	–	–	24	–	52	–	6	–	[29]
24.	Soya bean	–	0	–	12	–	3	0	–	0	0	23	0	55	6	–	–	[3]
25.	Peanut kernel	–	–	–	11.4	0	2.4	–	–	2.7	1.3	48.3	–	32.0	0.9	4.0	–	[33]
26.	Peanut	–	0	–	11	–	2	1	–	2	1	48	0	32	1	–	–	[3]
27.	Hazelnutkernel	–	–	–	4.9	0.2	2.6	–	–	–	–	83.6	–	8.5	0.2	0	–	[33]
28.	Walnut kernel	–	–	–	7.2	0.2	1.9	–	–	–	–	18.5	–	56.0	16.2	0	–	[33]
29.	Almond kernel	–	–	–	6.5	0.5	1.4	–	–	–	–	70.7	–	20.0	0	0.9	–	[33]
30.	Olive kernel	–	–	–	5.0	0.3	1.6	–	–	–	–	74.7	–	17.6	0	0.8	–	[33]
31.	Coconut	48.8	19.9	–	7.8	0.1	3.0	–	–	–		4.4	–	0.8	0	65.7	8.9[b], 6.2[c]	[33]
32.	Choice white		1.57	0.36	22.04	5.03	9.95	0.14	0.56	–	–	42.45	–	13.17	0.97	0.29	–	[64]
33.	Poultry fat		0.57	0.26	22.76	8.37	5.36	0.00	0.45	–	–	42.07	–	17.14	1.07	0.22	–	[64]
34.	Yellow grease		0.70	0.00	14.26	1.43	8.23	0.33	0.48	–	–	43.34	–	26.25	2.51	0.47	–	[64]
35.	Babassu	48	16	–	10	–	2	–	–	–	–	14	–	5	–	–	5	[35]
36.	Cumaru	–		–	23	–	7	–	–	–	–	37	–	29	–	–	4	[35]
37.	Piqui	–		–	40	–	2	–	–	–	–	47	–	4	–	–	7	[35]
38.	Castor	–	–	–	1.1	0	3.1	–	–	–	–	4.9	–	1.3	0		Ricinoic acid 89.6	[33]
39.	Poppy seed	–	–	–	12.6	0.1	4.0	–	–	–	–	22.3	–	60.2	0.5	–	–	[33]
40.	Bay laurel leaf	26.5	4.5	–	25.9	0.3	3.1	–	–	–	–	10.8	–	11.3	17.6	31.0	–	[33]
41.	Wheat grain	–	0.4	–	20.6	1.0	1.1	–	–	–	–	16.6	–	56.0	2.9	1.8	11.4[b]	[33]
42.	Crambe	–	0	–	2	–	1	2	–	1	1	19	59	9	7	–	–	[3]
43.	Rice–bran	–	0.4–0.6	–	11.7–16.5	–	1.7–2.5	0.4–0.6	–	–	0.4–0.9	39.2–43.7	–	26.4–35.1	–	–	–	[56]
44.	Sal	–	–	–	4.5–8.6	–	34.2–44.8	6.3–12.2	–	–	–	34.2–44.8	–	2.7	–	–	–	[56]
45.	Mahua	–	-	–	16.0–28.2	–	20.0–25.1	0.0–3.3	–	–	–	41.0–51.0	–	8.9–13.7	–	–	–	[56]
46.	Neem	–	0.2–0.26	–	13.6–16.2	–	14.4–24.1	0.8–3.4	–	–	–	49.1–61.9	–	2.3–15.8	–	–	–	[56]
47.	Karanjia	–	–	–	3.7–7.9	–	2.4–8.9	–	–	–	1.1–3.5	44.5–71.3	–	10.8–18.3	–	–	–	[45]
48.	Camelina oil	–	–	–	5.4	–	2.6	0.25	16.8	1.4	–	14.3	2.9	2.9	38.4	–	–	[77]
49.	Andiroba	–	–	–	27	1	7	–	–	–	–	49	–	16	–	–	–	[29]
50	B. carinata crude oil	–	–	–	3.1	–	1.0	0.7	–	–	–	9.7	42.5	16.8	16.6	–	–	[37]
51	*Cuphea 6iscosissima*	4.81	6.84		3.33		0.15					1.37		2.05	0.13		4.19[a], 40.24[b], 36.90[c]	[80]

Table 6
Fatty acid composition of different methyl esters.

S. No.	Vegetable oil methyl ester	Fatty acid composition (wt.%)																	Reference
		1:0 and 2:0	14:0	10:0	12:0	16:0	16:1	18:0	20:0	20:1	22:0	24:0	18:1	22:1	18:2	18:3	16:1	Osa, U.k. and acids	
	Rhus succedanea Linn	–	–	–	–	25.4	–	–	–	–	–	–	46.8	–	27.8	–	–	–	[81]
	Annona reticulata Linn	–	1.0	–	–	17.2	–	7.5	–	–	–	–	48.4	–	21.7	–	4.2	–	[82]
	Ervatamia coronaria Stapf	–	0.2	–	–	24.4	–	7.2	0.7	0.2	0.2	–	50.5	–	15.8	0.6	0.2	uk 0.2	[83]
	Thevetia peruviana Merrill	–	–	–	–	15.6	–	10.5	0.3	–	0.1	–	60.9	–	5.2	7.4	–	–	[84]
	Vallaris solanacea Kuntze	–	–	–	–	7.2	–	14.4	1.8	–	0.4	0.5	35.3	–	40.4	–	–	–	[83]
	Balanites roxburghii Planch	–	–	–	–	17.0	–	7.8	–	–	–	–	32.4	–	31.3	7.2	4.3	–	[85]
	Basella rubra Linn	–	0.4	–	–	19.7	–	6.5	–	0.7	–	–	50.3	–	21.6	0.4	0.4	–	[86]
	Canarium commune Linn	–	–	–	–	29.0	–	9.7	–	–	–	–	38.3	–	21.8	1.2	–	–	[87]
	Cannabis sativa Linn	–	–	–	–	–	–	–	–	–	–	–	15.0	–	65.0	15.0		Osa5.0	[83]
	Celastrus paniculatus Linn	2.0&1.7	–	–	–	25.1	–	6.7	–	–	–	–	46.1	–	15.4	3.0	–	–	[88]
	Euonymus hamiltonianuis Wall	8.5	–	–	–	18.3	–	1.5	–	–	–	–	39.1	–	25.8	5.3	–	Uk 1.5	[83]
	Terminalia bellirica Roxb	–	–	–	–	35.0	–	–	–	–	–	–	24.0	–	31.0	–	–	osa 10.0	[83]
	Terminalia chebula Retz	–	–	–	–	19.7	–	2.4	0.6	–	0.2	–	37.3	–	39.8	–	–	–	[83]
	Vernonia cinerea Less	–	8.0	–	–	23.0	–	8.0	3.0	–	4.0	–	32.0	–	22.0	–	–	–	[83]
	Corylus avellana	–	3.2	–	–	3.1	–	2.6	–	–	–	–	88.0	–	2.9	–	–	Uk 0.2	[83]
	Momordica dioica Rox	–	–	–	–	10.2	–	16.9	–	–	–	–	9.2	–	8.8	–	–	e.a. 54.9	[89]
	Aleurites fordii Hemsl	–	–	–	–	–	–	–	3.0	–	–	–	6.5	–	9.0	–	–	e.a. 81.5	[82]
	Aleurites moluccana Wild	–	–	–	–	5.5	–	6.7	–	–	–	–	10.5	–	48.5	28.5	–	Uk 0.3	[82]
	Aleurites montana Wils	–	–	–	–	–	–	–	3.5	–	–	–	18.2	–	10.7	–	–	Osa 3.0 e.a. 64.6	[87]
	Croton tiglium Linn	–	11.0	–	–	1.2	–	0.5	2.3	–	–	–	56.0	–	29.0	–	–	–	[87]
	Euphorbia helioscopia Linn	–	5.5	–	2.8	9.9	–	1.1	–	–	–	–	15.8	–	22.1	42.7	–	Uk 0.1	[83]
	Jatropa curcas Linn	–	1.4	–	–	15.6	–	9.7	0.4	–	–	–	40.8	–	32.1	–			[90]
	Joannesia princeps Vell	–	2.4	–	–	5.4	–	–	–	–	–	–	45.8	–	46.4	–			[87]
	Mallotus phillippinensis Arg	–	–	–	–	3.2	–	2.2	–	–	–	–	6.9	–	13.6	–	–	K.a.72.0	[90]
	Putranjiva roxburghii	–	–	–	–	8.0	–	15.0	3.0	–	–	–	56.0	–	18.0	–	–	–	[87]
	Sapium sebiferum Roxb	–	4.2	–	0.3	62.2	–	5.9	–	–	–	–	27.4	–	–	–	–	–	[87]
	Hydnocarpus kurzii Warb	–	–	–	–	4.0	–	–	–	–	–	–	14.6	–	–	–	–	H.a.39.4 G.a.19.5 C.a.22.5	[90]
	Hydnocarpus wightiana Blume	–	–	–	–	1.8	–	–	–	–	–	–	6.9	–	–	–	–	H.a.48.7 G.a12.2 C. 27.0 H. 3.4	[90]
	Calophyllum apetalum Wild	–	–	–	–	8.0	–	14.0	–	–	–	–	48.0	–	30.0	–	–	–	[91]
	Calophyllum inophyllum Linn	–	–	–	–	17.9	2.5	18.5	–	–	–	2.6	42.7	–	13.7	2.1	–	–	[90]
	Garcinia combogia Desr	–	–	–	–	2.3	–	38.3	0.3	–	–	–	57.9	–	0.8	0.4	–	–	[90]
	Garcinia indica Choisy		–	–	–	2.5	–	56.4	–	–	–	–	39.4	–	1.7	–	–	–	[87]
	Garcinia echinocarpa Thw	–	–	–	–	3.7	–	43.7	–	–	–	–	52.6	–	–	–	–	–	[87]
	Garcinia morella Desr	–	–	–	–	0.7	–	46.4	2.5	–	–	–	49.5	–	0.9	–	–	–	[87]
	Mesua ferrea Linn	–	0.9	–	–	10.8	–	12.4	0.9	–	–	–	60.0	–	15.0	–	–	–	[90]
	Mappia foetida Milers	–	–	–	–	7.1	–	17.7	–	–	–	–	38.4	–	–	36.8	–	–	[87]
	Illicium verum Hook	–	4.43	–	–	–	–	7.93	–	–	–		63.24	–	24.4	–	–	–	[92]
	Saturega hortensis Linn	–	–	–	–	4.0	–	4.0	–	–	–		12.0	–	18.0	62.0	–	–	[83]
	Perilla frutescens Britton	–	–	–	–	–	–	–	–	–	–	–	9.8	–	47.5	36.2		Osa 6.5	[83]
	Actinodaphne angustifolia	–	1.9	4.3	87.9	0.5	–	–	–	–	–	–	5.4	–	–	–	–	–	[90]
	Litsea glutinosa Robins	–	–	–	96.3	–	–	–	–	–	–	–	2.3	–	–	–	–	U.k. 1.4	[89]
	Neolitsea cassia Linn	–	3.8	3.0	85.9	–	–	–	–	–	–	–	4.0	–	3.3	–	–	–	[93]
	Neolitsea umbrosa Gamble	–	11.5	1.7	59.1	–	–	–	–	–	–	–	21.0	–	6.7	–	–	–	[93]
	Michelia champaca Linn	–	–	–	–	20.7	–	2.5	2.6	–	–	–	22.3	–	42.5	–	6.9	U.K.2.5	[83]
	Hiptage benghalensis Kurz	–	–	–	–	2.6	–	1.6	2.6	–	–	–	4.5	–	4.4	–	–	R.a.84.3	[83]
	Aphanamixis polystachya Park	–	–	–	–	23.1	–	12.8	–	–	–	–	21.5	–	29.0	13.6	–	–	[82]
	Azadirachta indica	–	–	–	–	14.9	–	14.4	1.3	–	–	–	61.9	–	7.5	–	–	–	[92]
	Melia azadirach Linn	–	0.1	–	–	8.1	–	1.2	–	–	–	–	20.8	–	67.7	–	1.5	–	[87]
	Swietenia mahagoni Jacq	–	–	–	–	9.5	–	18.4	–	–	–	–	56.0	–	–	16.1	–	–	[87]
	Anamirta cocculus Wight & Hrn	–	–	–	–	6.1	–	47.5	–	–	–	–	46.4	–	–	–	–	–	[87]
	Broussonetia papyrifera Vent	–	–	–	–	4.0	–	6.1	3.0	–	–	–	14.8	–	71.0	1.0	–	–	[86]
	Moringa concanensis Nimmo	–	–	–	–	9.7	–	2.4	3.3	–	–	–	83.8	–	0.8	–	–	–	[86]
	Moringa oleifera Lam	–	–	–	–	9.1	–	2.7	5.8	–	–	–	79.4	–	0.7	0.2	2.1	–	[86]
	Myristica malabarica Lam	–	39.2	–	–	13.3	–	2.4	–	–	–	–	44.1	–	1.0	–	–	–	[87]

Table 6 (*Continued*)

S. No.	Vegetable oil methyl ester	Fatty acid composition (wt.%)																	Reference
		1:0 and 2:0	14:0	10:0	12:0	16:0	16:1	18:0	20:0	20:1	22:0	24:0	18:1	22:1	18:2	18:3	16:1	Osa, U.k. and acids	
	Argemone mexicana	–	0.8	–	–	14.5	–	3.8	1.0	–	–	–	18.5	–	61.4	–	–	–	[87]
	Pongamia pinnata Pierre	–	–	–	–	10.6	–	6.8	4.1	2.4	5.3	2.4	49.4	–	19.0	–	–	–	[90]
	Ziziphus mauritiana Lam	–	–	–	–	10.4	–	5.5	1.8	2.6	1.2	–	64.4	1.7	12.4	–	–	–	[83]
	Princepia utilis Royle	–	1.8	–	–	15.2		4.5	–	–	–	0.9	32.6	–	43.6	–	–	Uk1.4	[87]
	Meyna laxiflora Robyns	–	–	–	–	18.8		9.0	–	–	–	–	32.5	–	39.7	–	–	–	[89]
	Aegle marmelos correa Roxb	–	16.6	–	–	8.8	–	–	–	–	–	–	30.5	–	36.0	8.1	–	–	[82]
	Salvadora oleoides Decne	–	50.7	0.8	35.6	4.5	–		–	–	–	–	8.3	–	0.1	–	–	–	[90]
	Salvadora persica Linn	–	54.5	1.0	19.6	19.5	–		–	–	–	–	5.4	–		–	–	–	[90]
	Santalum album Linn	–	–	–	–	1.9	–	1.0	–	–	–	–	8.6	–	0.8	–	–	St.a.3.7 Sa.a.84.0	[83]
	Nephelium lappaceum Linn	–	–	–	–	2.0	–	13.8	34.7	4.2	–	–	45.3			–	–	–	[93]
	Sapindus trifoliatus Linn	–	–	–	–	5.4	–	8.5	20.7	–	2.1	–	55.1	–	8.2	–	–	–	[81]
	Schleichera oleosa Oken	–	–	–	–	1.6	–	10.1	19.7	–	4.0	–	52.5	0.9		–	–	G.a.8.4	[82]
	Madhuca butyracea Mac	–	–	–	–	66.0	–	3.5	–	–	–	–	27.5	–	3.0	–	–	–	[94]
	Madhuca indica JF Gmel	–	1.0	–	–	17.8	–	14.0	3.0	–	–	–	46.3	–	17.9	–	–	–	[95]
	Mimusops hexendra Roxb	–	–	–	–	19.0	–	14.0	1.0	–	–	–	63.0	–	3.0	–	–	–	[87]
	Quassia indica Nooleboom	–	–	–	–	9.0	–	–	–	–	–	–	36.0	–	48.0	–	–	osa7.0	[83]
	Ximenia americana Linn	–	–	–	–	–	–	1.2	–	–	–	–	60.8	–	6.7	–	–	Osa1.5 X.a.14.626:015.2	[83]
	Pterygota alata Rbr	–	–	–	–	14.5	–	8.5	–	–	–	–	44.0	–	32.4	–	–	Uk1.0	[85]
	Holoptelia integrifolia	–	3.5	–	–	35.1	–	4.5	1.4	–	–	–	53.3				1.9	Uk1.1	[83]
	Urtica dioica Linn	–	–	–	–	9.0	–	–	–	–	–	–	14.6		73.7	2.7	–	–	[96]
	Tectona grandis Linn	–	0.2	–	–	11.0		10.2	2.3	–	–	–	29.5		46.4	0.4	–	–	[87]

Osa: Other saturated acid; u.k.: unknown; e.a.: elaeostearic acid; K.a.: kamlolenic acid; H.a.: hydnocarpic acid; G.a.: gorlic acid C.a.: chaulmoogric acid; C.H.: chaulmoogric homolog; R.a.: ricinolic acid; St.a.: stearolic acid; Sa.a: santalbic acid; G.a.:gadoleic acid; X.a.:ximenic acid.

25 part of sunflower oil and 75 parts of diesel were blended as diesel fuel [100]. The low viscosity is good for better performance of engine, which decreases with increasing the percentage of diesel.

4.3. Microemulsion

A micro emulsion define as a colloidal equilibrium dispersion of optically isotropic fluid microstructure with dimensions generally into 1–150 range formed spontaneously from two normally immiscible liquids and one and more ionic or more ionic amphiphiles. [99] They can improve spray characteristics by explosive vaporization of the low boiling constituents in micelles [101,102]. The engine performances were the same for a microemultion of 53% sunflower oil and the 25% blend of sunflower oil in diesel [103]. A microemultion prepared by blending soyabean oil, methanol, and 2-octanol and cetane improver in ratio of 52.7:13.3:33.3:1.0 also passed the 200 h EMA test [104].

4.4. Transesterification

Transesterification (also called alcoholysis) is the reaction of a fat or oil with an alcohol to form esters and glycerol. A catalyst is usually used to improve the reaction rate and yield. Excess alcohol is used to shift the equilibrium toward the product because of reversible nature of reaction. For this purpose primary and secondary monohybrid aliphatic alcohols having 1-8 carbon atoms are used [105].

(a) *Chemistry of transesterification process*: Transesterification consist of a number of consecutive, reversible reactions [14,99]. The triglycerides are converted step wise to triglycerides, monoglyceride and finally glycerol. A mole of ester librated at each step (Fig. 3).

(i) *Alkali catalyzed transesterification*: In transesterification method we can use different catalyst. The reaction mechanism for alkali catalyzed transesterification was formulated in three steps [106] as explained in Fig. 4. The first step is an attack on the carbonyl carbon atom of the triglycerides molecule by the anion of the alcohol (Methoxide ion) to form a tetrahedral intermediate reacts with an alcohol (methanol) to regenerate the anion of alcohol (methoxide ion). In the last step, rearrangement of tetrahedral intermediate results in the formation of a fatty acid ester and a diglyceride. When NaOH, KOH, K_2CO_3 or other similar catalysts were mixed with alcohol, the actual catalysts, alkoxide group is formed [107]. Kim et al [108] have developed a process for the production of Biodiesel from vegetable oils using heterogeneous catalyst $Na/NaOH/Al_2O_3$. These catalysts showed almost the same activity under the optimized reaction conditions compared to conventional homogeneous NaOH catalyst. For an alkali catalyzed transesterification, the glycericed and alcohol must be substantially anhydrous [109] because water makes the reaction partially change to saponification, which produces soap.

A number of researchers have worked with feed stokes that have elevated FFA (free fatty acid) levels [61,110–113]. However, in most cases, alkaline catalysts have been used and the FFAs (Free fatty acids) were removed from the process stream as soap and considered waste. Waste greases typically contain from 10 to 25% FFAs. This is far beyond the level that can be converted to Biodiesel using an alkaline catalyst.

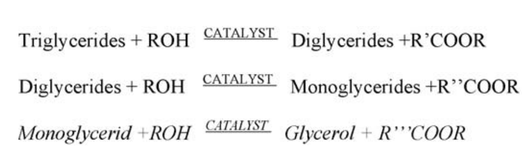


Fig. 3. Transestrification reaction.

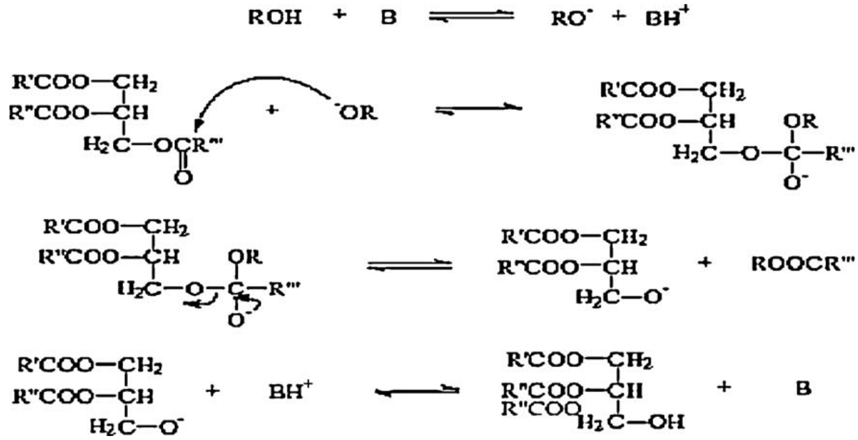


Fig. 4. Mechanism of the alkali-catalyzed transesterification of vegetable oils [106,107].

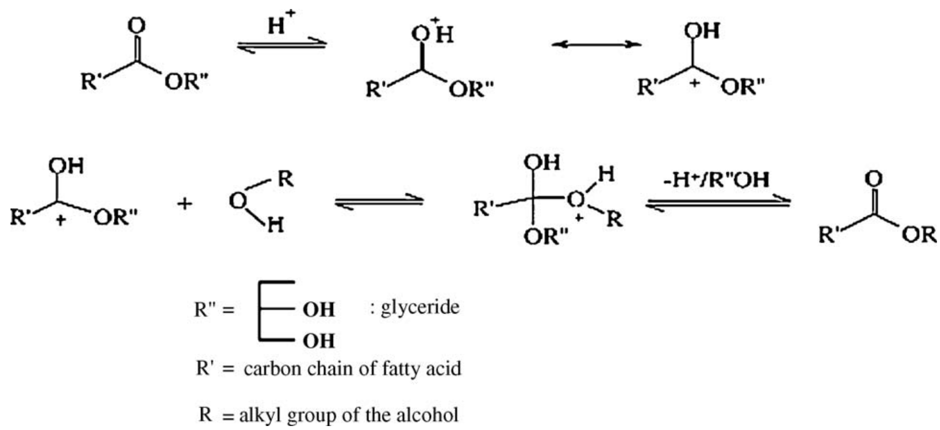


Fig. 5. Mechanism of acid catalyzed transesterification.

(ii) *Acid catalyst transesterification*: An alternative process is to use acid catalyst that some researchers have claimed are more tolerant of free fatty acids [114–116]. The mechanism of acid catalyzed transesterification of vegetable oil (for a monoglyceride) is shown in Fig. 5: However, it can be extended to di- and triglycerides. The protonation of carbonyl group of the ester leads to the carbocation, which after a nucleophilic attack of the alcohol produces a tetrahedral intermediate. This intermediate eliminates glycerol to form a new ester and to regenerate the catalyst. We can use acid alkali and biocatalyst in transesterification method. If more water and free fatty acids are in triglycerides, acid catalyst can be used [117]. Transemethylation occur approximately 4000 times faster in the presence of an alkali catalyst than those catalyzed by the same amount of acidic catalyst [118].

(iii) *Lipase catalyst transesterification*: This transesterification process is like alkali transesterification, only ratio of catalyst and solvent a stirring time different, and in this transesterification we have used lipase catalyst. The process is explained in the following Fig. 6.

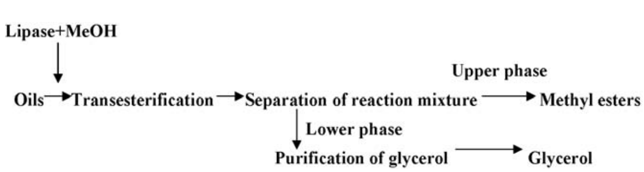


Fig. 6. Flow diagrams comparing biodiesel production using lipase-catalysis [30].

Lipases are known to have a propensity to act on long-chain fatty alcohols better than on short-chain ones [119]. Thus, in general, the efficiency of the transesterification of triglycerides with methanol (methanolysis) is likely to be very low compared to that with ethanol in systems with or without a solvent.

Various studied have been conducted for transesterification reaction for different catalyst, alcohol and molar ratios at different temperature. The results and experimental conditions of some studies are summarized in Tables 7 and 8.

Various types of alcohols – primary, secondary, and straight- and branched-chain – can be employed in transesterification using lipases as catalysts (Table 8). Linko et al. [128] have demonstrated the production of a variety of biodegradable esters and polyesters with lipase as the biocatalyst. In the transesterification of rapeseed oil with 2-ethyl-I-hexanol, 97% conversions of esters was obtained using *Candida rugosa* lipase powder. De et al. [129] investigated the conversion of fatty alcohol esters (C_4–$C_{18:1}$) using immobilized *Rhizomucor miehei* lipase (Lipozyme IM-20) in a solvent-free system. The percentage of molar conversions of all corresponding alcohol esters ranged from 86.8 to 99.2%, while the slip melting points of the esters were found to increase steadily with increasing alcohol chain length (from C_4 to C_{18}) and to decline with the incorporation of unsaturation for the same chain length (as from C_{18} to $C_{18:1}$). Transesterification of the triglycerides sunflower oil, fish oil, and grease with ethanol, *i.e.* ethanolysis, has also been studied. In each case, high yields beyond 80% could be achieved using the lipases from *M. miehei* [130], *Candida antarctica* [131], *Pseudomonas cepacia* [132], respectively. Nelson et al. [133]

Table 7
Transesterification method.

S. No.	Sample	Catalyst	Alcohol	Temperature	Ration to alcohol to oil	Result; Yields	Reference
1	Microalgae	Sulfuric acid	Methanol	30 °C	56:1	60%	[120]
2	Rice bran	Two-step acid-catalyzed Sulfuric acid	Methanol	60 °C	10:1	< 96%.	[121]
3	Karang oil	KOH,Solid acid catalysts viz. Hb; Zeolite,Montmorillonite K-10 and ZnO were also used	Methanol Tetrahydrofuran (THF), when used as a co solvent increased the conversion to 95%.	60 °C.	10:1	92%	[44]
4	Peanut oil	NaOH	Methanol	50 °C		90%	[122]
5	Soybean oil	Absence of catalyst.	Supercritical methanol, CO2 as co-solvent in the reaction system	280 °C	24 and CO_2/methanol = 0.1,	98%	[123]
6	Soybean oil	Solid super acid catalysts of sulfated tin and zirconium oxides and tungstated zirconia 2. noctanoic acid	Methanol	200–300 °C; 175–200 °C	20 h	90% for both	[124]
7	Sunflower oil	Supercritical fluids, Enzyme in supercritical carbon dioxide	Supercritical methanol and ethanol.	200–400 °C	40	(80–100%) (27–30%)	[125]
8	Canola oil	Two-stage process, KOH	Methanol	25 °C	6:1	87%	[126]
9	Sunflower frying oil	KOH	Methanol	25 °C	6:1	90%	[127]

investigated the abilities of lipases in transesterification with short-chain alcohols to give alkyl esters. The lipase from *M. miehei* was the most efficient for converting triglycerides to their alkyl esters with primary alcohols, whereas that from *C. antarctica* was the most efficient for transesterifying triglycerides with secondary alcohols to give branched alkyl esters. Maximum conversions of 94.8–98.5% for the primary alcohols methanol, ethanol, propanol, butanol, and isobutanol, and of 61.2–83.8% for the secondary alcohols isopropanol and 2-butanol were obtained in the presence of hexane as a solvent. In solvent-free reactions, however, yields with methanol and ethanol were lower than those obtained with hexane; in particular, the yield with methanol decreased to 19.4%. Mittelbach [134] reported transesterilication using the primary alcohols methanol, ethanol, and 1-butanol, with and without petroleum ether as a solvent. Although the ester yields with ethanol and 1-butanol were relatively high, even in reactions without a solvent, with methanol only traces of methyl esters were obtained. Abigor et al. [135] also found that in the conversion of palm kernel oil to alkyl esters using p *cepacia* lipase, ethanol gave the highest conversion of 72%, while only 15% methyl esters was obtained with methanol. Lipases are known to have a propensity to act on long-chain fatty alcohols better than on short-chain ones [119]. Thus, in general, the efficiency of the transesterification of triglycerides with methanol (methanolysis) is likely to be very low compared to that with ethanol in systems with or without a solvent.

5. Properties of alternative fuel or diesel

5.1. Properties of oil

The vegetative oils are mainly characterized by some fuel related properties. Some of them are listed in Table 9 [3,139]. The kinematics viscosity of vegetable oils varies in the range of 30–40 cSt at 38 °C. High viscosity of these oils is due to large molecular mass and chemical structure. The fatty acid methyl esters of seed oils and fats have already been found suitable for use as fuel in diesel engine [140] because transesterification provides a fuel viscosity that is close to that diesel.

Vegetable oils have high molecular weights in the range of 600–900, which are three or more times higher than diesel fuels. The volumetric heating values of these oils are in the range of 39–

Table 8
Enzymatic transesteritication reactions using various types of alcohols and lipases.

S.N.	Oil	Alcohol	Lipase	Conversion (%)	Solvent	Ref.
1	Rapeseed	2-Ethyl-1-hexanol	*C. rugosa*	97	None	[128]
2	Mowrah, Mango, Kernel, Sal	C, -C, alcohols	*M. miehei* (Lipozyme IM-20)	86.8–99.2	None	[129]
3	Sunflower	Ethanol	*M. meihei* (Lypozyme)	83	None	[130]
4	Fish	Ethanol	*C. anturctica*	100	None	[131]
5	Recycled restaurant Grease	Ethanol	*J. cepacia* (Lipase PS-30) + *C. anturclica* (Lipase SP435)	85.4	None	[132]
6	Tallow, Soybean, Rapeseed	Primary alcohols a; Secondary alcohols b A-Methanol, ethanol, propanol, butanol, and isobutanol. B-Isopropanol and 2-butanol	*M. miehei* (Lipozyme IM60) *C. antarctica* (SP435) *M. miehei* (Lipozyme IM60) *M. miehei* (Lipozyme IM60)	94.8–98.5; *61.2–83.8*; 19.4–65.5	Hexane; Hexane; None; None	[133]
7	Sunflower	Methanol; Methanol; Ethanol	*P. juorescens*	3; 79; 82	None; Petroleum; ether None	[134]
8	Palm kernel; Oil	Methanol; Ethanol	*I. cepuciu* (Lipase PS-30)	15; 72	None; None	[135]
9	Soybean oil	Methanol	*Rhizomucor miehei* (Lipozyme IM-77) enzyme amount 0.9 BAUN	92.2%	Molar ratio 3.4:1,	[136]
10	Soybean oil	Methanol	*C. antarctica* lipase	93.8%	>1/2 molar equivalent MeOH	[137]
11	Sunflower oil	Methanol	*Pseudomonas fluorescens* (Amano AK)	(>90%)	oil:methanol (1:4.5)	[16]
12	Palm oil	Methanol	*Rhizopus oryzae*	55% (w/w)	Water	[138]

Table 9
Oils characteristics.

Vegetable oil	Kinematic viscosity at 38 °C (mm^2/s)	Cetane No. (°C)	Heating Value (MJ/kg)	Cloud Point (°C)	Pour Point (°C)	Flash Point (°C)	Density (kg/l)	Carbon residue (wt.%)
Corn	34.9	37.6	39.5	−1.1	−40	277	0.9095	0.24
Cottonseed	33.5	41.8	39.5	1.7	−15	234	0.9148	0.24
Crambe	53.6	44.6	40.5	10.0	−12.2	274	0.9048	0.23
Linseed	27.2	34.6	39.3	1.7	−15.0	241	0.9236	0.22
Peanut	39.6	41.8	39.8	12.8	−6.7	271	0.9026	0.24
Rapeseed	37.0	37.6	39.7	−3.9	−31.7	246	0.9115	0.30
Safflower	31.3	41.3	39.5	18.3	−6.7	260	0.9144	0.25
Sesame	35.5	40.2	39.3	−3.9	−9.4	260	0.9133	0.24
Soya bean	32.6	37.9	39.6	−3.9	−12.2	254	0.9138	0.25
Sunflower	33.9	37.1	39.6	7.2	−15.0	274	0.9161	0.27
Palm	39.6	42.0	–	31.0	–	267	0.9180	0.23
Babassu	30.3	38.0	–	20.0	–	150	0.9460	–
Diesel	3.06	50	43.8	–	−16	76	0.855	–

40 MJ/kg, which are low, compared to diesel fuels (about 45 MJ/kg). The presence of chemically bound oxygen in vegetable oils lowers their heating values by about 10%. The cetane numbers are in the range of 34–42. The cloud and pour points of vegetable oils are higher than that of diesel fuels.

5.2. Properties of Biodiesel

The characteristics of Biodiesel are close to diesel fuels, and therefore Biodiesel becomes a strong source to replace the diesel fuels. The conversion of triglycerides into methyl or ethyl esters through the transesterification process, reduces the molecular weight to one-third that of the triglyceride and also reduces the viscosity by a factor of about eight and increases the volatility marginally. Biodiesel has viscosity close to diesel fuels. These esters contain 10–11% oxygen by weight, which may encourage more combustion than hydrocarbon-based diesel fuels in an engine. The cetane number of Biodiesel is around 50. The use of tertiary fatty amines and amides can be effective in enhancing the ignition quality of the finished diesel fuel without having any negative effect on its cold flow properties. Since the volatility increases marginally, the starting problem persists in cold conditions. Biodiesel has lower volumetric heating values (about 12%) than diesel fuels but has a high cetane number and ash point (Table 10).Chiu [145] reported the cold flow properties of Biodiesel (B100) and 80% (B80) to 90% Biodiesel in kerosene were evaluated with pour point depressants, toward the objective of identifying approaches to transport and mix Biodiesel with diesel in cold climates. Four cold flow improver additives were tested at 0.1–2% in B80, B90, and B100 blends. Two additives significantly—a mixture of 0.2% additives, 79.8% Biodiesel, and 20% kerosene reduced the pour point of B100 by 27 °C. The unrefined Biodiesels showed higher lubricity properties than refined Biodiesel. The chemical factors influencing the lubricity properties of Biodiesels were investigated by Hu et al. [146]. Methyl ester and monoglycerides are the main composition that determines the lubricity of Biodiesel that meets international standards. Free fatty acids and diglycerides can also affect the lubricity of Biodiesel, but not so much as monoglycerides.

Biodiesel is considered clean fuel it has no sulphur no aromatics and has about 10% built in oxygen, which helps it to burn fully its higher cetane number improves the ignition quality even when blended in the petroleum diesel.

It is a general property of hydrocarbons that the auto-ignition temperature is higher for more volatile hydrocarbons. Therefore, the less volatile middle distillate fractions of crude oil boiling in the range of 250–370 °C are suitable as diesel fuels. The hydrocarbons present in the diesel fuels include parafins, naphthenes, olefins and aromatics. Carbon numbers of these hydrocarbons ranges from 12 to 18.

5.3. Determination and measurement methods for oil/Biodiesel properties

The properties of the methyl esters were determined by methods specified in the Handbook of Analytical Methods for Fatty Acid Methyl Esters as Diesel Substitutes [147] or by equivalent standard methods, which given in Table 11.

A considerable amount of experience exists in the U.S. with a 20% blend of Biodiesel with 80% diesel fuel (B20). Although Biodiesel (B100) can be used, blends of over 20% Biodiesel with diesel fuel should be evaluated on a case-by-case basis until further experience is available [148]. Table 12 shows the Comparison of properties of diesel and Biodiesel Acid value, viscosity and density were determined according to ISO 660, 3104 and 3675, respectively. Ash content, cloud point and pour point were measured using BS 2000, cold filter plug point (CFPP) using BS 6188 and iodine value using DIN 53241. Total and free glycerine were

Table 10
Physical properties of Biodiesel.

Vegetable oil methyl ester	Kinematic viscosity (mm^2/s)	Cetane no.	Lower heating value (MJ/kg)	Cloud point (°C)	Pour point (°C)	Flash point (°C)	Density (kg/l)	Reference
Peanut	4.9 (37.8 °C)	54	33.6	5	–	176	0.883	[141]
Soya bean	4.5 (37.8 °C)	45	33.5	1	−7	178	0.885	[142]
Babassu	3.6 (37.8 °C)	63	31.8	4	–	127	0.875	[126]
Palm	5.7 (37.8 °C)	62	33.5	13	–	164	0.880	[143]
Sunflower	4.6 (37.8 °C)	49	33.5	1	–	183	0.860	[141]
Tallow	–	–	–	12	9	96	–	[30]
Rapeseed b	4.2 (40 °C)	5 l–59.7	32.8				0.882 (15 °C)	[144]
Palm b	4.3-4.5(40 °C)	64.3–70	32.4	–	–	–	0.872–0.877 (15 °C)	[144]
Soybean b	4.0 (40 °C)	45.7-56	32.7	–	–	–	0.880 (15 °C)	[144]
Diesel	3.06	50	43.8	–	−16	76	0.855	
20% BD blend	3.2	51	43.2	–	−16	128	0.859	

Table 11
ASTM specifications (D6751) for B100.

Property	ASTM Method	Limits	Units
Flash Point	D93	130 min	°C
Water & Sediment	D2709	0.050 max	%vol.
Kinematic Viscosity (40 °C)	D445	1.9–6.0	mm^2/s
Sulfated Ash	D874	0.020 max.	%mass
Sulfur	D5453.	0.05 max	%mass
Copper Strip Corrosion	D130	No. 3 max.	
Cetane	D613	47 min	
Cloud Point	D2500	Report	°C
Carbon Residue (100% Sample)	D4530[a]	0.050 max	% mass
Acid Number	D664	0.80 max	Mg KOH/g
Free Glycerin	D6584	0.020 max	%mass
Total Glycerin	D6584	0.240 max	%mass
Phosphorous Content	D4951	0.001 max	%mass
Distillation Temperature, Atmospheric Equivalent Temperature (90% Recovered)	D1160	360 max	°C

[a]The carbon residue shall be run on the 100% sample.

determined enzymatically [147]. Methanol content was measured by gas chromatography using a Porapak Q column (Perkin-Elmer Ltd., Beaconsfield, Buckinghamshire), 900 mm × 3 mm at 90 °C, injector at 110 °C, 25 ml/min nitrogen flow, and flame ionization detector. Lubricating oils were screened for the presence of methyl esters by thin-layer chromatography [150,151]. If detected they were determined quantitatively by following the method: lubricating oil (5 g) was saponified [152] and the molar amount of methyl ester in the oil was calculated from the difference in titre volumes between the original and used oils. The percentage of methyl ester in the used oil was determined by dividing the molar amount in the used oil by the molar amount in 5 g methyl ester, also determined by saponification.

6. Performance of alternative fuel (oil and Biodiesel) as a fuel

6.1. Use of oils as fuel and their performance

Many researchers have concluded that vegetable oils hold promise as alternative fuels for diesel engines [3,4]. During World War II Seddon [153] experimented with using several different vegetable oils in Perkins P-6 diesel engine with great success and concluded that vegetable oils could be used to power a vehicle under normal operating conditions. However it was noted that much more work was needed before vegetable oils used as a reliable substitute for diesel fuel. Bruwer et al. [154] studied the use of sunflower seed oil as a renewable energy source. When operating tractor with 100% sunflower oil instead of diesel fuel, an 8% power loss occurred after 1000 h of operation, which was corrected by replacing the fuel injector, and injector pump. Yarbrough et al. [155] reported that raw sunflower oils were found to be unsuitable fuel, while refined sunflower oil was found to be satisfactory. Tahir et al. [156] reported that oxidation of sunflower oil left heavy gum and wax deposit on tested tractor, which could lead to engine failure. Bettis et al. [157] and Engler et al. [158] reported that the sunflower seed oil is acceptable only for short-term use as a fuel source but long term durability test indicated sever problems due to carbonization of combustion chamber. Goering et al. [159] studied the characteristic properties of eleven vegetable oils to determine which oil would be best suited for use as an alternative fuel source. Bacon et al. [160] evaluated the use of several vegetable oils as potent fuel sources and reported that use of these oils caused carbon build up in the combustion chamber. Schoedder [161] used rapeseed oil as a diesel fuel replacement in Germany with mixed results. Short-term engine tests indicated similar energy outputs in both rapeseed oil and diesel fuel. Initial long-term engine tests showed that difficulties arose in engine operation after 100 h due to deposits on piston rings, valves and injectors. Auld et al. [162] analyze rapeseed oil and showed a relationship between viscosity and fatty acid chain length. Bettis et al. [157] reported that rapeseed oil contained 94–95% of the energy content of diesel fuel, and to be approximately 15 times viscous. Reid et al. [163] evaluated chemical and physical properties of 14 vegetable oils. They pointed out that the oils are very differently from petroleum-based fuel because of ‘high viscosity’. Engine test showed that carbon deposits in the engine were reduced if the oil was heated prior to combustion. It was also noted that carbon deposit levels differed from oils with similar viscosities because of oil composition.

Table 12
Comparison of fuel properties between diesel and Biodiesel.

Fuel Property	Diesel	Biodiesel
Fuel Standard	ASTM D975	ASTM PS 121
Fuel composition	C10-C21 HC	C12-C22 FAME
Lower Heating Value (Btu/gal)	131,295	117,093
Kin. Viscosity, @ 40 °C	1.3–4.1	1.9–6.0
Specific Gravity kg/l @ 60 °F	0.85	0.88
Density, lb/gal @ 15 °C	7.079	7.328
Water, ppm by wt.	161	0.05% max
Carbon (wt.%)	87	77
Hydrogen (wt.%)	13	12
Oxygen, by dif. wt.%	0	11
Sulfur (wt.%)	.05 max	0.0 - 0.0024
Boiling Point (°C)	188-343	182-338
Flash Point (°C)	60-80	100-170
Cloud Point (°C)	-15 to 5	-3 to 12
Pour Point (°C)	-35 to -15	-15 to 10
Cetane Number	40-55	48-65
Stoichiometric Air/Fuel Ratio (w/w)	15	13.8
BOCLE Scuff (g)	3,600	>7,000
HFRR (μm)	685	314

Source: [149].

6.2. Need of blending and its effect on performance

Engelman et al. [164] reported that 10–50% soybean oil fuel blends with diesel minimize the carbon deposition in combustion chamber. Quick [165] used over 30 different vegetable oils to operate compression engines and reported that the use of raw vegetable oil fuels can lead to premature engine failure. Blending vegetable oils with diesel fuel was found to be a method to reduce chocking and extend engine life. Sims et al. [166] indicated that short-term engine tests with 50% vegetable oil fuel blend had no adverse effects. Carbon deposits on combustion chamber components was found to be approximately same as that found in engines operated on 100% diesel fuel. The similar results were reported by Bartholomew [167], Barsic and Humke [168], Fort et al. [169], Baranescu and Lusco [170], Worgetter [171], Wanger and Peterson

[172] and Vander Walt and Hugo [173] working on different oils such as pea nut oil, cottonseed oil, sunflower oil, rapeseed oil, and sun flower oil respectively. German et al. [174] reported that carbon deposits on the internal engine components were greater for the tractor fueled with 50/50 sunflower oil/diesel than those fueled with a 25/75 sunflower/diesel fuel blend. Sapaun et al. [175] reported that power out puts were nearly the same for palm oil, blend of palm oil and diesel fuel, and 100% diesel fuel. Short-term using of palm oil fuel showed no adverse effects. Hofman et al. [176] and Peterson et al. [177] indicated that while vegetative oil fuel blends had encouraging results in short term testing, problems occurred in long term durability tests. Pestes and Stanislao (1984) [178] used a one to one blend of vegetable oil and diesel fuel to study the piston rings deposits. Premature piston ring sticking and carbon built up due to the use of the one to one fuel blend caused engine failure. These investigators suggested that to reduce piston ring deposits a fuel additive or a fuel blend with less vegetative oil was needed. The atomization and injection characteristic of vegetative oils were significantly different from that of diesel fuel due to the higher viscosity of the vegetative oils [179]. Engine performance tests showed that power output slightly decreased when using vegetable oil fuel blends. Nag et al. [180] showed that performance tests using fuel blend as great as 50–50 seed oil from the Indian Ambulate plant and diesel fuel exhibited no loss of power. Knock free performance with no observable carbon deposits on the functional parts of the combustion chamber were observed during these tests. McCutchen [181] compared engine performance of direct injection engine to indirect injection engines when fueled with 30% soybean oil 70% diesel fuel. The result showed that indirect injection could be operated on this fuel blend while the direct injection engine could not without catastrophic engine failure occurring. The direct injection engines showed injector coking and piston ring sticking as a result of using sunflower oil. McDonnell et al. [182] studied the use of a semi-refined rapeseed oil as a diesel fuel extender. Test results indicated that the rapeseed oil could serve as a fuel extender at inclusion rates up to 25%. As a result of using rapeseed oil as a fuel, injector life was shortened due to carbon build up.

6.3. Use of esters as fuel and their performance

Usta [54] showed that tobacco seed oil methyl ester can be partially substituted for the diesel fuel at most operating conditions in term of performance parameter and emissions without any engine modification and preheating of the blends. Frohlich and Rice [37] reported that in vehicle testes, the reduction in fuel economy with camellia methyl ester did not lead to a more rapid deterioration of the lubricating oil. Kalligeros et al. [183] reported that the engine was fueled with pure marine diesel fuel and blends containing two types of Biodiesel, at proportion up to 50%, the performance was satisfactory. Monyem and Van Gerpen [184] evaluated the impact of oxidized Biodiesel on engine performance and emission. A John Deere 4276 turbocharged DI diesel engine was fueled with oxidized and unoxidized Biodiesel and the performance and emission were compared with No. 2 diesel fuel. The engine performance of the neat Biodiesels and their blends was similar to that of No. 2 diesel fuel with the same thermal efficiency, but higher fuel consumption. Machacon et al. [185] studied the operation of the test engine with pure coconut oil and coconut oil diesel fuel blends for a wide range of engine load condition was shown to be successful even without engine modification. It was also shown that increasing the amount of coconut oil in the coconut oil—diesel fuel blend resulted in lower smoke and NO_x emission. Tan [26] estimated reduction in net CO_2 emission at 77–104 g/MJ of diesel replaced by Biodiesel. He predicted reduction in CO_2 emission which are much greater than values reported in recent studied on Biodiesel derived from other vegetable oils, due to both the large amount of potential fuel in the residual biomass and to the lower energy input the traditional coconut farming techniques. Wang [186] shown that the heavy trucks fueled by B35 emitted significantly lower particulate matter (PM) and moderately lower carbon monoxide (CO) and hydrocarbon (HC) than the same trucks fueled by number 2 diesel (D2). Oxides of nitrogen (NO_x) emission from B35 and D2, however, were generally in the same level. Clark et al. [187] reported that the derivatives particularly the methyl esters of rapeseed, soybean and other seed oils have been shown to be similar to diesel fuel in performance. Mittelbach et al. [188] examined that the exhaust from combustion of the vegetative oil esters is lower in carbon monoxide and particulate content but higher in nitrogen oxide than diesel fuel. Peterson et al. [112] used ethyl ester of rapeseed as a Biodiesel and reported that no problems or unusual events were encountered with the truck's operation. The truck was completely unmodified as to the engine and fuel system. However, the Biodiesels were considerably less volatile than the conventional diesel fuel. Peterson et al. [6] stated that the Biodiesel esters can be used directly or as blends with diesel fuel in a diesel engine.

Kalam and Masjuki [52] evaluate the effect of anticorrosion additive in Biodiesel isolated from palm as a palm ester on diesel engines, performance, emission and wear characteristics. Cardone et al. [36] used the non-food use of *Brassica carinata* oil for Biodiesel production. The Biodiesel, produced by transesterification of the oil extracted from the *Brassica carinata* seeds, displayed physical–chemical properties suitable for the use as diesel car fuel. Raheman and Phadatare [43] used the blend of the *Pongamia pinnata* methyl ester and diesel to evaluate the diesel engine emissions and performance and found reduction in exhaust emission together with increase in torque, brake power, brake thermal efficiency and reduction in brake-specific, fuel consumption. The blends of *Pongamia pinnata* esterifide oil is a suitable alternative fuel for diesel and could help in controlling air pollution. Carraretto et al. [189] checked the operation of a Biodiesel fueled boiler for some months and stated that the Biodiesel seems to be a promising solution for boilers with only minor adjustments and the performances are comparable with oil operation. Carbon monoxide emission is reduced but no NO_3 are increased. Shi et al. [190] prepared blend of 20% (v/v) ethanol/methyl soyate and observed that particulate matters decreased with increasing oxygenate content in the fuel but nitrogen oxide (NO_x) emission increased. Spataru and Romig [191] and Schumacher and Bolgert [192] both studied several blends of No. 2 diesel and SME or canola methyl ester (CME) to determine and compare engine emission from the Detroit Diesel corporation (DDC) 6V92TA engine (a type of diesel engine widely used in transit buses and heavy trucks) operated on those fuels. Grabaski et al. [193] also employed a 1991 DDC series 60 engine to determine emission of NO_x, CO, HC, and PM that result from blending Biodiesel (methyl soy ester) and conventional diesel. The test showed that as the percentage of Biodiesel blend in fuel increased, the NO_x increased but HC, CO, and PM decreased. Schumacher and Peterson [191,194] both conducted about 100,000 mi of road test on Cummins B5 9L engine running on 100% Biodiesel in Dodge pickups. No fuel related problems were noted during the tests on the modification trucks. Both emission test results showed that CO, HC, and smoke exhaust emission from Biodiesel tend to be lower. Chang et al. [195] studied the effects of using blends of methyl and isopropyl ester of soybean oil with no 2 diesels at several steady state operational conditions in a four-cylinder turbocharged John Deer 4276T engine. Both methyl and isopropyl ester provided significant reductions in PM emission as compared with no. 2 diesel fuels. Emission of CO, and HC were also reduced significantly, but NO_x increased by about 12%. The fatty acid methyl esters of seed oils and fats and have already been found

suitable for use as fuel in diesel engine [140] because transesterification provides a fuel viscosity that is close to that diesel fuel. In India the prohibitive cost of edible oils prevent their use in Biodiesel, but non edible oils are affordable for Biodiesel production. The main commodity sources for Biodiesel in India can be non-edible oils obtained from plant species such as *Jatropha curcas* (ratanjyot), *Pongamia pinnata* (Karanj), *Callophyllum inophyllum* (Nagchampa), *Hevca brasiliensis* (Rubber), etc. Biodiesel can be blended at any level with petroleum diesel to create a Biodiesel blend or can be use in its pure form just like petroleum diesel. The diesel engines operated by Biodiesel are required very little or low engine modification because Biodiesel has properties similar to petroleum diesel fuels. It can be stored just like a petroleum diesel fuel and hence does not require separate infrastructure.

7. Problems arises and their solution during the use of alternative fuels

7.1. Problem arises during the use of oil

There are many problems associated with direct use of oil in engine. A potential solution has been given to overcome from these problems caused by use of vegetative oil at the place of petroleum diesel (Table 13).

These effects can be reduced or eliminated using filtered, frying oil and the blend of 95% used cooking oil and 5% diesel fuel [196]. Due to their high viscosity (about 11–17 times higher than diesel fuel) and low volatility, they do not burn completely and form deposits in the fuel injector of diesel engines [33]. Different ways have been considered to reduce the high viscosity of vegetable oils:

(a) dilution of 25 parts of vegetable oil with 75 parts of diesel fuel,
(b) microemulsions with short chain alcohols such as ethanol or methanol,
(c) thermal decomposition, which produces alkanes, alkenes, carboxylic acids,
(d) catalytic cracking, which produces alkanes, cycloalkanes and alkylbenzenes, and
(e) transesterification with ethanol or methanol.

7.2. Problem arises during the use of Biodiesel

The technical disadvantages of Biodiesel/fossil diesel blends include problems with fuel freezing in cold weather, reduced energy density, and degradation of fuel under storage for prolonged periods. One additional problem is encountered when blends are first introduced into equipment that has a long history of pure hydrocarbon usage. Hydrocarbon fuels typically form a layer of deposits on the inside of tanks, hoses, etc. Biodiesel blends loosen these deposits, causing them to block fuel filters. However, this is a minor problem, easily remedied by proper filter maintenance during the period following introduction of the Biodiesel blend [200].

The disadvantages of Biodiesel are:

- Constraints on the availability of agricultural feedstock impose limits on the possible contribution of Biodiesels to transport.
- The kinematic viscosity is higher than diesel fuel. This affects fuel atomization during injection and requires modified fuel injection systems.
- Due to the high oxygen content, it produces relatively high NO_x levels during combustion.
- Oxidation stability is lower than that of diesel so that under extended storage conditions it is possible to produce oxidation products that may be harmful to the vehicle components.
- Biodiesel is hygroscopic. Contact with humid air must be avoided.
- Production of Biodiesel is not sufficiently standardised. Biodiesel that is outside European or US standards can cause corrosion, fuel system blockage, seal failures, filter clogging and deposits at injection pumps.
- The lower volumetric energy density of Biodiesel means that more fuel needs to be transported for the same distance travelled.
- It can cause dilution of engine lubricant oil, requiring more frequent oil change than in standard diesel-fueled engines.
- A modified refuelling infrastructure is needed to handle Biodiesels, which adds to their total cost.

8. Economic viability of Biodiesel

Biodiesel has become more attractive recently because of its environmental benefits and the fact that it is made from renewable resources. The remaining challenges are its cost and limited availability of fat and oil resources. There are two aspects of the cost of Biodiesel, the costs of raw material (fats and oils) and the cost of processing. The cost of raw materials accounts for 60–75% of the total cost of Biodiesel fuel [98].

Table 13
Known problems, probable cause and potential solutions for using straight vegetable oil in diesels engine [22].

Problem	Probable cause	Potential solution
Short-term Cold weather starting	High viscosity, low cetane, and low flash point of vegetable oils	Preheat fuel prior to injection. Chemically alter fuel to an ester
Plugging and gumming of filters, lines and injectors	Natural gums (phosphatides) in vegetable oil. Other ash	Partially refine the oil to remove gums. Filter to 4-μm
Engine knocking	Very low cetane of some oils. Improper injection timing	Adjust injection timing. Use higher compression engines. Preheat fuel prior to injection. Chemically alter fuel to an ester
Long-term Coking of injectors on Piston and head of engine	High viscosity of vegetable oil, incomplete combustion of fuel. Poor combustion at part load with vegetable oils	Heat fuel prior to injection. Switch engine to diesel fuel when operation at part load. Chemically alter the vegetable oil to an ester
Carbon deposits on Piston and head of engine	High viscosity of vegetable oil, incomplete combustion of fuel. Poor combustion at part load with vegetable oils	Heat fuel prior to injection. Switch engine to diesel fuel when operation at part loads. Chemically alter the vegetable oil to an ester
Excessive engine wear	High viscosity of oil, incomplete combustion of fuel. Poor combustion at part load with vegetable oils. Possibly free fatty acids in vegetable oil. Dilution of engine lubricating oil due to blow-by of vegetable oil	Heat fuel prior to injection Switch engine to diesel fuel when operation at part loads. Chemically alter the vegetable oil to an ester. Increase motor oil changes. Motor oil additives to inhibit oxidation
Failure of engine lubricating oil due to Polymerization	Collection of polyunsaturated Vegetable oil blow-by in crankcase to the point where polymerization Occurs vegetable oil to an ester. Increase motor oil changes. Motor oil additives to inhibit oxidation	Heat fuel prior to injection. Switch engine to diesel fuel when operation at part load. Chemically alter the

The use of used cooking oil can lower the cost significantly. However, the quality of used cooking oils can be bad [198]. Studies are needed to find a cheaper way to utilize used cooking oils to make Biodiesel fuel. There are several choices, first removing free fatty acids from used cooking oil before transesterification, using acid catalyzed transesterification, or using high pressure and temperature [199]. In terms of production cost, there also are two aspects, the transesterification process and by-product (glycerol) recovery. A continuous transesterification process is one choice to lower the production cost. The foundations of this process are a shorter reaction time and greater production capacity. The recovery of high quality glycerol is another way to lower production cost. Because little water is present in the system, the Biodiesel glycerol is more concentrated. Unlike the traditional soap glycerol recovery process, the energy required to recover Biodiesel glycerol is low due to the elimination of the evaporation process. In addition, the process is also simpler than soap glycerol recovery since there is a negligible amount of soap in Biodiesel glycerol. This implies that the cost of recovering high quality glycerol from Biodiesel glycerol is lower than that of soap glycerol and that the cost of Biodiesel fuel can be lowered if a Biodiesel plant has its own glycerol recovery facility. With the increase in global human population, more land may be needed to produce food for human consumption (indirectly via animal feed). So insufficient land may also increase the production cost of Biodiesel plants. The problem already exists in Asia where vegetable oil prices are relatively high. The same trend will eventually happen in the rest of the world. This is the potential challenge to Biodiesel production. Biodiesel can be used most effectively as a supplement to other energy forms. Biodiesel is particularly useful in mining and marine situations where lower pollution levels are important. Biodiesel also can lower US dependence on imported petroleum based fuel.

9. Conclusion

In recent years, Biodiesel has become more attractive as an alternative fuel for diesel engines because of its environmental benefits and the fact that it is made from renewable resources. Several methods available for producing Biodiesel, transesterification of natural oils and fats are currently the method of choice. The purpose of the process is to lower the viscosity of the oil or fat. Researchers focused mainly the edible oils to produce the Biodiesel because of easily availability and familiarity. Very few researchers concentrated on Non edible oil for the same purpose. Non-edible oils can also be utilized for making Biodiesel fuel. For the production of Biodiesel fuel, an alkali-catalysis process has been established that gives high conversion levels of oils to methyl esters. Enzymatic processes using both extra cellular and intracellular lipases have recently been developed. The cost of lipase production is the main hurdle to commercialization of the lipase-catalyzed process; several attempts have been made to develop cost-effective systems. In terms of production cost, there also are two aspects, the transesterification process and by-product (glycerol) recovery. A continuous transesterification process is one choice to lower the production cost. The foundations of this process are a shorter reaction time and greater production capacity. The recovery of high quality glycerol is another way to lower production cost. Land may be a cost increasing factor for Biodiesel production, because of more and more land required to live the growing population. To overcome the land problem, the high yielding Biodiesel plants (non edible producing plants) should be grown in marginal and waste land areas.

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